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THERMAL POLYMERIZATION OF ACETYLENE
IN THE PRESENCE OF POROUS FILLERS

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The aromatics formed from acetylene, according to the process described, would serve as effective antiknock ingredients when added to liquid fuel, particularly aviation fuel. Conversion of kerosene, according to Tatarinov's method, is specifically mentioned, as far as the production of acetylene is concerned. Within the scope of the petroleum and natural-gas industry, methane is an additional crude material for the production of acetylene, and consequently may be converted into aromatics by way of the acetylene.

The polymerization of acetylene proceeds with a decrease of volume; therefore, increased pressure should assist the formation of the product. However, since acetylene already explodes at a comparatively slight excess pressure (1), the use of high pressures is limited.

Zelinskiy (2) proposed that indirect pressure be substituted for direct by forcing heated acetylene to pass through a porous substance with an extensively developed surface. Using activated carbon for this purpose, Zelinskiy succeeded in obtaining a polymerization product with a yield of 70-74% by weight, with reference to acetylene. This product contained up to 35% of benzene and 4% of toluene.

These results were considerably better than those which were reached before Zelinskiy's time by other investigators (3, 4, 5), and thus Zelinskiy's hypothesis in regard to the favorable effect of activated carbon on the process of thermal polymerization of acetylene seemed to find experimental verification. However, certain authors (6, 7, 8) have pointed out that the porosity of the carbon has no

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essential significance, since results have been obtained with less porous substances, such as coke, caolin, pumice, brick, and porcelain, which are similar to those obtained with activated carbon or silica gel. In the opinion of the above authors, the actual catalyst of the polymerization is the carbon formed on the surfaces of the different fillers during the thermal process.

Fischer (9), and also Lozovoy (10), have observed that resin formation begins only after 5-6 hours of warming up of the activated carbon. According to Fisher, during the warming-up process there is formed on the activated carbon a film of carbon which is the actual catalyst of the polymerization reaction.

In the opinion of Lozovoy (10), it is difficult to decide whether this carbon is the actual catalyst or whether it is a product of far-advanced condensation [polymerization accompanied by dehydrogenation], and does not affect the process.

Works of other investigators provide no answer to this question, although it was noted (10, 11, 12) that when a dense, shiny layer (crust) of carbon is formed, the polymerization of acetylene proceeds intensively, while in cases when a sooty carbon formed in the reaction space and there was an insignificant yield of resin, acetylene decomposed into its elements.

Experimental Part

The raw material for polymerization was gas produced by the decomposition of kerosene in an electric-arc discharge, according to the Tatarinov method (13, 14). This gas has the following percentage composition:

Acetylene	33.1%
Ethylene	8.7
Ethane	1.0
Methane	8.3
Hydrogen	45.4
Carbon monoxide	0.6
Propene and n-butene	2.9

The polymerization was carried out in a circulating system consisting of a porcelain tube heated by a circular electrical furnace, condensers, scrubbers, and receptacles for reaction products and gas. The temperature was measured by a thermocouple placed in a porcelain sheath inside the reaction tube. The rate of gas flow was measured by a gasometer and a rheometer.

The gaseous reaction products were analyzed for O₂, CO, CO₂, and saturated hydrocarbons by the customary methods of gas analysis. Olefinic hydrocarbons were determined by Dobryanskiy's sulfuric-acid method (15), as modified by Markovich and Dement'yeva (16). Butadiene was analyzed with maleic anhydride, according to Korotkov.

The products in the receptacles and the light hydrocarbons which were distilled with steam from the scrubber oil were separated first into two fractions boiling above and below 200° respectively, and then the fraction boiling below 200° was further fractionated into the narrower 70-90, 100-120, and 125-150° fractions in which the content of the respective aromatic hydrocarbons was determined.

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Experiments in an Unfilled Porcelain Tube

Both the temperature and the time during which the material being polymerized is present in the reaction zone, i.e., the time of contact, are of considerable importance. The fact that many investigators have not considered the time factor has often led to erroneous conclusions and has made it more difficult to compare different results. Therefore, we have striven for a strict calculation of the time of contact and have been attentive that it should be the same in experiments run for comparison.

The contact period τ in seconds is calculated from the formula (18):

$$\tau = \frac{vT'}{FT''},$$

where v is the volume of the heated part of the reaction tube in ml; T' is the absolute temperature of the input gas; T'' is the absolute temperature of the heated gas inside the reaction tube; and F is the volumetric rate of gas flow in ml/sec, which is equal to the average of the volumes of the input and output gases:

$$F = \frac{V_0 + V_k}{2}.$$

This assumes a linear variation of the gas volume along the reaction tube. As Vvedenskiy showed (19), the volume varies by a more complex law, but, since in our experiments acetylene is two thirds diluted by other gases whose volume varies little, the error arising from this simplification is insignificant.

To select the optimum temperature, a series of experiments was conducted with a constant rate of gas flow of one l/min in a porcelain tube whose diameter was 32 mm and whose heated portion was 800 mm in length.

The polymerization had already started at 400°, and the yield of products reached its maximum of 65.8% at 700°. Above 700°, the yield of tar began to decrease sharply. The temperature also had an effect on the qualitative composition of the products. Thus, no aromatic hydrocarbons were formed at 400°, while at 500° benzene appeared, and its quantity increased continuously as the temperature increased. Toluene appeared at 600°, but with a further increase of the temperature its yield began to fall off, which is apparently explained by secondary reactions of demethylation and condensation into ditolyl.

The optimum time for the passage of acetylene through the heated zone was 12 seconds. With a shorter contact period, a large portion of the acetylene did not enter into reaction, while with a longer period the yield of light tar fractions decreased and the yield of heavy tars and coke increased.

Polymerization of Acetylene Gas in the Presence of Fillers

We were most of all interested in finding out how the process would go when the reaction tube was charged with a filler of the same material as the tube. For this purpose, we used porcelain rings of 6 x 6 x 3 mm in size. These rings occupied 45% of the useful volume of the reaction space (20), which was taken into consideration in determining the contact period.

The results of experiments conducted with this filler under the same time and temperature conditions as for the empty porcelain tube showed that for equal times of contact both the degree of decomposition of acetylene and the yields of liquid, gaseous, and solid products remained practically the same. Small deviations were observed in the composition of both gas and tar.

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Thus, porcelain as a filler manifests no effect on the polymerization of acetylene, but the use of a filler in the tube slightly improves the conditions of heat transfer and reduces the danger of local overheating and of the resulting decomposition of acetylene.

Silica Gel and Activated Carbon as Fillers

When silica gel was used as a filler in the reaction tube, it was well dried and the individual pieces had an average dimension of 4-5 mm. The free volume of the tube, allowing for the porosity of silica gel, was about 75% of the original, and this was taken into account in determining the time of contact.

The experiments, conducted each time with a fresh charge of catalyst, showed that the yield of polymerization products not only did not increase, as is indicated in literature (2, 10), but decreased considerably. Thus, at 700°, when the time of contact was 35.2 seconds, only 16.9% by weight of products, with reference to the initial acetylene, were formed.

Neither by reducing the time of contact as a constant temperature of 700° nor by reducing the temperature could the yield be raised to its former level.

The same situation develops with activated carbon. Here we should point out the high degree of conversion of acetylene. Thus, at 600°, up to 90% of the acetylene enters into the reaction, and at 700°, all of the acetylene reacts.

If the yields of both the gas and the polymerization products are considered, then we find in one experiment, to give a typical example, that the gas which formed comprised 50.56% and the polymerization products 9.65% by weight of the gas used, i.e., a total amount which was considerably less than the initial quantity of gas could be accounted for.

The remaining 39.79% obviously ought to be sought in the carbon deposited in the form of coke or soot in the reaction tube. However, only about 3 g, or 4% of [loose]coke was collected, while the weight of the silica gel increased by 33.54 g, comprising 34.5% by weight of the original gas, or 65.5% by weight of the acetylene used. Consequently, a large part of the acetylene was converted into products of far-advanced condensation which settled in the silica-gel pores. Therefore, it could be expected that, as heavy condensation products accumulated in the pores of the silica gel, its porosity would have to decrease up to the point where all the pores were plugged. At that point neither silica gel nor activated carbon should differ markedly in its effect on the polymerization from such comparatively nonporous substances as porcelain, clay, glass, etc. This hypothesis was fully supported by experiments in which the same silica gel was used for a prolonged period and was only taken out periodically to determine its increase in weight.

These experiments, conducted at 700° with a contact period of 17.5 sec, show that the yield of liquid polymerizates increases with the time during which the silica gel is left in the reaction tube, and after 22.5 hours reaches 67% by weight of the initial acetylene and remains at this level. On the other hand, the yield of heavy condensation products decreases in proportion to the increase of the yield of liquid products from 54% at the beginning of the experiment to 12% after 23 hours. If more acetylene is passed through, the yield of heavy condensation products changes little and comprises 10-11% by weight of the acetylene passed through.

Thus, in the beginning stages of the reaction in the presence of porous fillers, the major part of the acetylene is converted into heavy condensation products which are deposited in the pores of the filler and gradually fill

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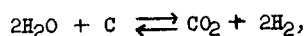
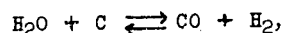
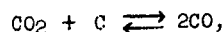
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them completely. After all the pores have been filled, the yield and composition of all the products are stabilized in time and do not differ from the yield and composition of the products formed in an unfilled tube or in a tube charged with a porcelain filler. The carbon crust deposited on the surface of the filler increases continuously as more acetylene is passed through and at the same time reduces the free volume of the reaction space and, consequently, the contact period. If the experiment is of sufficient duration, the contact period becomes shorter than the minimum (12 sec) required for maximum conversion of acetylene into liquid products. Finally, there comes the moment when the reaction tube becomes completely plugged up.

Considering the above-mentioned facts, it is not difficult to explain why the yield of polymerization products begins to decrease after optimum conditions of the warming up of the silica gel have been attained, and why the output of these products increases again if CO₂ (9) or steam (11) is passed for a short time through the tube filled with silica gel. The answer here lies not in the poisoning of a supposed catalyst, i.e., the deposit of a layer of carbon on the silica gel, and its regeneration, as Fisher (9) proposes, but in the simple oxidation of carbon:



as a result of which carbon in the form of CO and CO₂ goes out of the reaction zone together with the gaseous products, and the available cross section is increased. Carbon monoxide was detected in the gases from the process by both Fisher (9) and Berl (11) and coauthors.

We think it relevant to emphasize in conclusion that in Zelinskiy's experiments (2) the same activated carbon served as a filler for 40 hours and that Lozovoy (10), in repeating Zelinskiy's experiments, worked the whole time with the same carbon without renewing it. Thus, in neither Zelinskiy's nor Lozovoy's experiments was the activated carbon really a porous substance.

In the polymerization of acetylene, we collected 713 g of liquid products, from which the following substances were separated and determined exactly: benzene with a yield of 30.4%; toluene with a yield of 5.5%; naphthalene with a yield of 8.05%; and styrene in a quantity corresponding to less than 1% of the weight of the products.

Conclusions

1. The polymerization of acetylene is accompanied by the formation of heavy condensation products which are deposited on the surfaces of the reaction vessel in the form of a carbonaceous mass. This carbon does not catalyze the polymerization of acetylene, but is a necessary product of the acetylene's conversion.

2. Porous substances with highly developed surfaces, such as carbon and silica gel during the initial stages of thermal processing, promote the formation of heavy polymerization products, which are deposited in the pores of these substances.

After the pores have been plugged up, which takes 10-20 hr, the action of silica gel and activated carbon does not differ from the action of such fillers as porcelain, clay, and glass, whose role amounts to an improvement of the conditions of heat transfer.

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